# New $CO_2$ Laser Lines in the 11-$\mu$m Wavelength Region: New Hot Bands

Che-Chung Chou, K. M. Evenson, K. R. Zink, A. G. Maki, and Jow-Tsong Shy

*Abstract*—**Nineteen new laser lines in the 11-$\mu$m wavelength region have been observed in cw oscillation from a $CO_2$ laser with a high-$Q$, high-resolution cavity at a higher than usual current density. The frequency of each line has been measured using heterodyne frequency measurement techniques. Analysis of the frequencies showns that 15 lines are rotation-vibration transitions of the $01^12$-$[11^11, 03^11]_I$ band (the first sequence hot band) of the $CO_2$ molecule and four lines belong to the rotation-vibration transitions of the $02^21$-$[12^20, 04^20]_I$ band of $CO_2$.**

## I. Introduction

NINETEEN new laser lines in the 11-$\mu$m wavelength region have been observed in *cw* oscillation from a $CO_2$ laser using a 100 line/mm grating. These new lines occured between the relatively strong 11-$\mu$m hot-band lines which oscillate to $J = 55$ in the $P$-branch. Some of them show the closely spaced doublets characteristic of high-$J$ transitions of hot bands and fifteen of these were assigned as "sequence hot-band" lines, $01^12$-$[11^11, 03^11]_I$ (see Fig. 1) while four were assigned to another hot band, $02^21$-$[12^20, 04^20]_I$ (see Fig. 1). The identity of both sets of transitions has been verified by comparing our heterodyne frequencies with those calculated from molecular constants [1]–[3].

Fig. 1 shows the main 10-$\mu$m and 9-$\mu$m bands of the $CO_2$ laser. The sequence bands involve upper state levels with $v_3 > 1$. They are not easy to observe for two reasons. First, the gain of the sequence bands is relatively small due to the lower population of the initial vibrational levels [4], [5]. Second, since the anharmonicities of the vibrations of a $CO_2$ molecule are very small, the frequencies of the sequence lines are usually very close to those of the fundamental bands (regular band or hot band). If the laser cavity does not have sufficient frequency discrimination, then the fundamental bands will dominate as a result of gain competition.

To overcome these limitations, several methods have been developed to obtain the sequence lines. The most effective way is the addition of an intracavity hot $CO_2$ absorption cell [6] to absorb the radiation at the normal laser transition frequencies. Reid and Siemsen [7] used this technique to observe lasing of the first sequence bands, $00^02$-$[10^01, 02^01]_{I,II}$. Solodukin [8] observed sequence lines by using a double-pass non-Littrow-mounted grating in the laser cavity. We increased the frequency resolution by using a grating with a higher groove density and by adding a ribbed tube to inhibit the waveguide (or wall-bounce) modes. Using this combination, we recently observed the 9-$\mu$m hot-band lines, $01^11$-$[11^10, 03^10]_I$ [9].

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## II. Experimental Details

The $CO_2$ laser which we used for the observation of these 11-$\mu$m sequence hot-band lines was the same as that used in [9] except we replaced the 171 line/mm grating with a 100 line/mm grating. A grating with a lower density of grooves avoided the nearly grazing incidence in the 11-$\mu$m wavelength region, which would introduce extra cavity loss. The 100 line/mm grating had 1% zero-order output coupling at 11-$\mu$m. The 1.5 m laser cavity was formed by the Littrow-mounted grating and a gold-coated 10-m radius-of-curvature end mirror and had no Brewster windows. The zeroth order reflection from the grating was used as the laser output. The laser tube was ribbed with 1.3-mm internal ribs spaced every 10 mm and had a minimum diameter of 13.5 mm. The discharge was divided in half and used two cathodes at the center separated by 10 cm. It had an active length of 1.34 m. The use of the ribbed tube increased the wavelength discrimination by about a factor of three.

Since the resolving power of the grating used here was lower than the resolving power of the grating used in [9], we did not see any 9-$\mu$m hot-band lines. The frequency gap between the 9- and 10-$\mu$m regular bands is closed by this laser's oscillation on regular band lines with $J$ up to 66 of the 9-$\mu$m $P$-branch and $J$ up to 62 of the 10-$\mu$m $R$-branch.

We first used a gas mixture of 10% $CO_2$, 12% $N_2$, and 78% He at a total pressure of 1.9 kPa (14 Torr) and a discharge current of 70 mA in each half of the laser. Under these conditions, the power of the sequence hot-band lines was typically 400 mW. We increased the laser power by adding more $N_2$ to the laser gas mixture; for example, with 9% $CO_2$, 20% $N_2$, and 71% He at a total pressure of 1.5 kPa (11 Torr), and a discharge current of 71 mA in each half, the output power of P(38) of the $01^12$-$[11^11, 03^11]_I$ band increased from 400 to 550 mW. The $01^12$-$[11^11, 03^11]_I$ band (as with other sequence bands) required more excitation of the higher $v_3$ vibrational levels. However, since the discharge current of our laser strongly depends on the gas pressure, we could not make a systematic parametric study on the output power.

The frequency measurements were made by heterodyning each hot-band line with a corresponding reference line from another $CO_2$ laser, using a MIM diode as the mixer. Regular

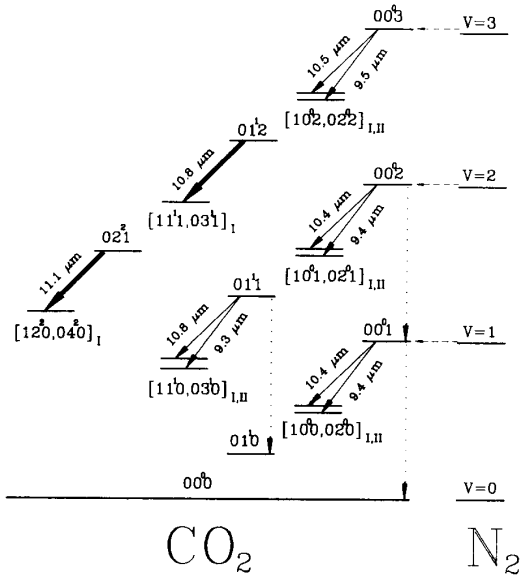


Fig. 1. Simplified vibrational energy level diagram of the $CO_2$ and $N_2$ molecules with arrows showing the lasing bands. The new lasing bands are shown by the extra heavy arrows. The dotted arrows show the 4.3 $\mu$m fluorescence for the frequency stabilization.

lines of a $^{13}C^{16}O_2$ laser, locked to the saturation-dip of the 4.3 $\mu$m fluorescence [10], were used as reference lines. Although the hot-band lines and the first sequence-band lines can be frequency locked to the saturation-dip of the 4.3 $\mu$m fluorescence (see Fig. 1) by using a longitudinal-type fluorescence collecting cell [11], [12], this scheme cannot be applied to the $01^12$-$[11^11,03^11]_I$ band because the lower level does not have sufficient population. The $02^21$-$[12^20,04^20]_I$ band suffers from insufficient power to saturate the absorption needed for the fluorescence stabilization. Therefore, the lines in each band were tuned to the peak of their gain profiles for each measurement and had an uncertainty of a few megahertz. The beat frequencies were generated in the MIM diode by beating the two lasers with the output of a microwave synthesizer and then were measured with a RF spectrum analyzer. The results are shown in Table I.

TABLE I
THE MEASURED FREQUENCIES OF THE NEWLY OBSERVED LASER LINES

| $J$ | $^{13}C^{16}O_2$ REF. | $\nu-\nu_{REF}$ [a] [MHz] | Obs. Freq. [MHz] | Obs.−Calc. [b] [MHz] |
|---|---|---|---|---|
| | | $01^{1e}2$-$[11^{1e}1,03^{1e}1]_I$ | | |
| P(45) | 10P(34) | -6 252 | 26 500 928 | 0.2 |
| P(43) | 10P(32) | 372 | 26 563 825 | -0.6 |
| P(41) | 10P(30) | 6 821 | 26 625 953 | -0.1 |
| P(39) | 10P(26) | -41 400 | 26 687 314 | 0.7 |
| P(37) | 10P(24) | -34 711 | 26 747 910 | 1.0 |
| P(35) | 10P(24) | 25 121 | 26 807 742 | -0.9 |
| P(31) | 10P(18) | -15 681 | 26 925 133 | -1.9 |
| P(29) | 10P(16) | -9 674 | 26 982 699 | 1.7 |
| | | $01^{1e}2$-$[11^{1e}1,03^{1e}1]_I$ | | |
| P(44) | 10P(32) | -11 692 | 26 551 761 | -0.7 |
| P(42) | 10P(30) | -6 534 | 26 612 598 | 1.6 |
| P(40) | 10P(26) | -55 970 | 26 672 744 | -0.9 |
| P(38) | 10P(26) | 3 495 | 26 732 209 | 0.1 |
| P(34) | 10P(20) | -39 580 | 26 849 090 | 0.6 |
| P(32) | 10P(20) | 17 838 | 26 906 508 | -0.7 |
| P(30) | 10P(16) | -29 124 | 26 963 249 | 0.0 |
| | | $02^{2f}1$-$[12^20,04^20]_I$ | | |
| P(25) | 10P(42) | 22 529 | 26 298 635 | -0.3 |
| P(23) | 10P(38) | -39 081 | 26 353 763 | -3.2 |
| P(21) | 10P(38) | 15 360 | 26 408 204 | 3.5 |
| | | $02^{2e}1$-$[12^20,04^20]_I$ | | |
| P(20) | 10P(36) | -15 076 | 26 435 235 | -0.1 |

[a] The reference frequencies used here are from L. D. Bradley, K. L. Soohoo, and C. Freed, IEEE J. Quantum Electron. QE-22, 234(1986).
[b] The molecular constants listed in Tables 2 and 3 below were used to obtain the calculated frequencies.

TABLE II
MOLECULAR CONSTANTS (IN MHz) USED TO FIT THE $01^12-[11^11,03^11]_I$ TRANSITIONS

| Molecular Constants | this work | Ref. 1 | Ref. 2 |
|---|---|---|---|
| $\nu_0$ | 27 733 334.7(47)[a] | | |
| $B(f)'$ | 11 545.906(7) | 11 545.868(3) | |
| $D(f)'\times10^3$ | 4.076(3) | 4.058 9(9) | |
| $B(f)''$ | [11 639.034 8][b] | | 11 639.034 8 |
| $D(f)''\times10^3$ | [3.612 26] | | 3.612 26 |
| $B(e)'$ | 11 528.371(7) | 11 528.450(6) | |
| $D(e)'\times10^3$ | 4.002(3) | 4.022 9(9) | |
| $B(e)''$ | [11 612.832 9] | | 11 612.832 9 |
| $D(e)''\times10^3$ | [3.694 49] | | 3.694 49 |

[a] The uncertainty in the last digits is given in parentheses. If the uncertainties and correlation of the lower state constants were taken into account, the true uncertainties in the constants determined by the present measurements would be larger.
[b] Values enclosed in square brackets were fixed during the least-squares fit.

## III. ANALYSIS OF THE MEASUREMENTS

### *The* $01^12$-$[11^11,03^11]_I$ *Sequence Hot Band*

Although this band had not been directly measured before this work, Bailly *et al.* [1] have given the ro-vibrational constants for the upper state while Esplin and Rothman [2] have given the constants for the lower state. Bailly [13] has recently given constants for the lower state $[11^11,03^10]_I$ that are slightly different. Yet another slightly different set of lower state constants were given by Bailly and Rossetti [14]. Our measurements are not extensive enough to determine all the necessary constants for both the upper and lower states, particularly because only $P$-branch transitions were measured. Consequently, we have fixed the lower state constants to the values given by Esplin and Rothman. The observed 15 transitions were then fit to the five constants $\nu_0, B(e)', D(e)', B(f)'$, and $D(f)'$. In this fit we used the term expressions

$$E(v,J) = G_v + B_v[J(J+1)] - D_v[J(J+1)]^2$$

and

$$\nu_0 = G'_v - G''_v,$$

which were used by Bailly *et al.* [1] and by Esplin and Rothman [2]. The results of the fit are shown in Table II. The constants given by Bailly *et al.* [1] are also given in Table II for comparison with the present results. The agreement is quite good and shows that our assignment of the transitions is consistent with the earlier measurements [1], [2].

The band center given by the present analysis is 925.084 47 ± 0.000 16 $cm^{-1}$ which is close to the value 925.0858 $cm^{-1}$ derived from several different band centers given in the literature. The band center given by this analysis is an extrapolated value and may not be as accurate as the uncertainty suggests.

TABLE III
MOLECULAR CONSTANTS (IN MHz) USED TO FIT THE $02^21$-$[12^20,04^20]$I TRANSITIONS

| Molecular Constants | this work | Ref. 1 | Ref. 3 |
|---|---|---|---|
| $\nu_0$ | 26 937 756.9(14)[a] | | |
| $B(f)'$ | [11 651.035 2][b] | 11 651.035 2(30) | |
| $D(f)'\times10^3$ | [4.119 15] | 4.119 15(150) | |
| $B(f)''$ | [11 738.270 2] | | 11 738.270 2(60) |
| $D(f)''\times10^3$ | [3.824 41] | | 3.824 41(180) |
| $B(e)'$ | [11 651.035 2] | 11 651.035 2(30) | |
| $D(e)'\times10^3$ | [4.093 07] | 4.093 07(150) | |
| $H(e)'\times10^8$ | [-0.680 5] | -0.680 5(270) | |
| $B(e)''$ | [11 738.270 2] | | 11 738.270 2(60) |
| $D(e)''\times10^3$ | [4.250 12] | | 4.250 12(300) |

[a] The uncertainty in the last digits is given in parentheses. The uncertainty in the band center given by this analysis is unrealistically small because it assumes that the rotational constants are all precisely known.
[b] Values enclosed in square brackets were fixed during the least-squares fit.

### *The* $02^21$-$[12^20,04^20]_I$ *Band*

Bailly *et al.* [1] have also given the constants for the upper state of this band and Bailly and Legay [3] have given the lower state constants. A more recent paper by Bailly [13] gives slightly different constants for the upper state but the uncertainty is slightly larger. For the analysis of the four measured transitions, the constants for both the upper and lower states were fixed at the literature values and only the band center was allowed to float in the least-squares fit. The constants used in this analysis are given in Table III.

This analysis gave a band center of 898.546 95 $cm^{-1}$, which can be compared with the value 898.548 38 $cm^{-1}$ determined from the sum and difference of several different band centers given in the literature. The cumulative error in the literature values used in this determination is certainly within the uncertainty of the present measurements and we are confident that the vibrational assignment is correct. No direct observation of this band has been reported before the present measurements.

## IV. CONCLUSION

We have made what we think is the first observation of laser oscillation of the $CO_2$ molecule on the $01^12$-$[11^11,03^11]_I$ and $02^21$-$[12^20,04^20]_I$ bands. Although only nineteen new lines are reported here, it may be possible to obtain more lines oscillating on the $01^12$-$[11^11,03^11]_I$ band by using a gas mixture with a higher nitrogen concentration and using an intracavity hot $CO_2$ absorption cell. With our recently observed 9-$\mu$m hot-band lines [9] and the 11-$\mu$m sequence hot-band lines of this work, the line density of the $CO_2$ laser has been dramatically increased.

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